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Halogen Oxidation of Some Group VI Metal Carbonyl Derivatives

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Halogen oxidation of several amine chromium and amine molybdenum carbonyls has been studied. The species isolated were $Cr(CO)_3(amine)X_2$, $Mo(CO)_4(amine)X_2$, $Mo(CO)_3(amine)_2X_2$, $Mo(CO)_2(amine)_2X_2$ and $[Mo(CO)_3(amine)_3X]X$ (X = halogen). (1-Diphenylphosphino-2-diphenylarsinoethane)metal tetracarbonyls (metal = Cr, Mo, W) after reaction with halogens gave $[Cr(CO)_4$(1-diphenylphosphino-2-diphenylarsinoethane)I]I, $M(CO)_3$(1-diphenylphosphino-2-diphenylarsinoethane)X_2 (M = Mo, W; X = Br, I) and $M(CO)_2$(1-diphenylphosphino-2-diphenylarsinoethane)Cl_2 (M = Mo, W). The complexes have been identified by microanalysis, infrared spectra and conductivity measurements.

Introduction

Although metal carbonyl halides are known from a fairly long time, they have become the subject of renewed interest in recent years. Two general methods have been suggested for the preparation of the substituted derivatives of group VI metal halocarbonyls and a number of neutral, cationic and anionic complexes have been synthesised. The first method deals with the halogen oxidation[1–6] of substituted derivatives of group VI metal carbonyls while the second one involves the action of ligands[7–10] on dihalotetracarbonylmetal(II) complexes. In our earlier communication[11] we have reported the halogenation of some aminetungsten penta- and bis(amine)tungsten tetracarbonyls. In this paper the work has been extended using several chromium and molybdenum amine carbonyls; peculiar results have been obtained on the halogenation of chromium complexes. Attempt has also been made to prepare the halogen derivatives of $M(CO)_4$(1-diphenylphosphino-2-diphenylarsinoethane) (M = Cr, Mo and W).

Results and Discussion

Halogenation of Amine Metal Pentacarbonyls

The halogen oxidation of amine molybdenum pentacarbonyls with one equivalent of bromine or iodine at room temperature in inert solvents like hexane or benzene under nitrogen yielded heptacoordinated $Mo(CO)_4(amine)X_2$ (amine = $C_4H_9NH_2$, $C_6H_5CH_2NH_2$, $C_6N_{11}NH_2$, $C_5H_{11}N$, C_4H_9NO; X=Br, I). On using excess of bromine or iodine, unidentified sticky products were obtained. In spite of several attempts these products could not be purified. Similar reactions with chlorine (dissolved in benzene) gave less stable products.

All the complexes were brown or orange in colour. They were insoluble in aliphatic hydrocarbons and light petroleum (60°–80° C) but dissolved in other common organic solvents with decomposition. In oxygenated solvents the decomposition was rapid and simultaneous evolution of carbon monoxide took place. They were nonelectrolytes in benzene. Their infrared spectra exhibited three very strong and one medium to weak shoulder bands in the CO region when measured in KBr discs (Table I). The C–O frequencies in these complexes were slightly in the higher region than their tungsten analogues.[11] The fourth band which varied in intensity in molybdenum complexes was not visible in the spectra of tungsten derivatives. The C–O frequencies in these halogenated complexes are in the order: chloro complexes ~ bromo complexes > iodo complexes.

The halogen oxidation of amine chromium pentacarbonyls did not yield the heptacoordinated $Cr(CO)_4(amine)X_2$ derivatives. On mixing the reactants at room temperature no change was observed. On warming the reaction mixture up to 50 °C, brown turbidity appeared in the reaction mixture. Evaporation of solvent *in vacuo* gave a brown solid which began to decompose into a green product during the course of isolation. The brown product was extracted in benzene as described in the Experimental. In the IR spectra of the extracted products in benzene two strong absorption bands appeared in the CO region. A weak or shoulder band also appeared in several cases (Table II). Their dilute solutions in benzene showed nonconductive behaviour. With the analogy of the spectral data of known compounds we presumed the stoichiometry of chromium derivatives as hexacoordinate, $Cr(CO)_3(amine)X_2$ (amine = $C_6H_{11}NH_2$, $C_5H_{11}N$, C_4H_9NO; X = Br, I).

TABLE I. C–O Stretching Frequencies and Molar Conductivity Data of $Mo(CO)_4(amine)X_2$ Derivatives.

Complex	CO Bands (KBr discs) (cm^{-1})				Mol. Cond. (benzene) ($ohm^{-1} cm^2$)
$Mo(CO)_4(C_4H_9NH_2)I_2$	2082s	2018s	1980s	1920s	<1
$Mo(CO)_4(C_6H_5CH_2NH_2)I_2$	2082s	2016s	1980s	1918s	<1
$Mo(CO)_4(C_6H_{11}NH_2)I_2$	2078s	2018s	1980s	1908s	<1
$Mo(CO)_4(C_4H_9NO)I_2$	2080s	2020s	1962s	1924sh	<1
$Mo(CO)_4(C_5H_{11}N)I_2$	2078s	2020s	1978s	1920sh	<1
$Mo(CO)_4(C_6H_5CH_2NH_2)Br_2$	2085s	2032s	1980s	1952s	<1
$Mo(CO)_4(C_6H_{11}NH_2)Br_2$	2092s	2022s	1962s	1920sh	<1
$Mo(CO)_4(C_4H_9NO)Br_2$	2092s	2024s	1954s	1920sh	<1
$Mo(CO)_4(C_5H_{11}N)Br_2$	2098s	2024s	1950s	1918sh	<1
$Mo(CO)_4(C_4H_9NO)Cl_2$	2092ms	2010s	1950sbr		<1
$Mo(CO)_4(C_5H_{11}N)Cl_2$	2090s	2018s	1950s	1924mw	<1

TABLE II. CO Stretching Frequencies of $Cr(CO)_3(amine)X_2$ Derivatives.

Complex		CO Bands (benzene) (cm^{-1})	
$Cr(CO)_3(C_6H_{11}NH_2)I_2$	1987vs,br	1894w	1823s,br
$Cr(CO)_3(C_4H_9NO)I_2$	1985s,br	1833s,br	
$Cr(CO)_3(C_5H_{11}N)I_2$	1992ms	1952s	1814s
$Cr(CO)_3(C_6H_{11}NH_2)Br_2$	1978s	1824sh	1802s
$Cr(CO)_3(C_4H_9NO)Br_2$	1980s	1838sh	1818s
$Cr(CO)_3(C_5H_{11}N)Br_2$	1985s	1836s	

Halogenation of Bis(amine)molybdenum Tetracarbonyls

In the halogenation reactions solid bis(amine)molybdenum tetracarbonyls were used and a solution of bromine or iodine was added dropwise onto the solid tetracarbonyls. The colour of the bromine or iodine solutions discharged immediately after the addition and solid bis(amine)molybdenum tetracarbonyls began to dissolve. In case of iodination the precipitation of $Mo(CO)_3(amine)_2I_2$ derivatives took place immediately after the dissolution of solid tetracarbonyls. These products were filtered, washed several times with hexane and dried *in vacuo*. The IR spectra of these complexes showed three strong bands in the C–O region (Table III).

TABLE III. C–O Stretching Frequencies of $Mo(CO)_3(amine)_2I_2$ and $Mo(CO)_2(amine)_2Br_2$ Derivatives.

Complex	CO Bands (cm^{-1})		
$Mo(CO)_3(C_6H_{11}NH_2)_2I_2$	2004s	1922s	1908s[a]
$Mo(CO)_3(C_4H_9NO)_2I_2$	2000s	1954s	1932s[a]
$Mo(CO)_3(C_5H_{11}N)_2I_2$	2010s	1932s	1914s[a]
$Mo(CO)_2(C_6H_{11}NH_2)_2Br_2$	1980s	1834s[b]	
$Mo(CO)_2(C_5H_{11}N)_2Br_2$	1965s	1824s[b]	

[a] KBr. [b] C_6H_6.

The brominated products were sticky in nature and could not be dried in spite of best efforts. The resemblance of the IR spectra of these products in benzene with the spectra of other known $Mo(CO)_2L_2X_2$ derivatives showed them to be the hexacoordinated Mo $(CO)_2(amine)_2X_2$ derivatives. In their IR spectra only two CO stretching bands were recorded (Table III).

Halogenation of Tris(amine)molybdenum Tricarbonyls

Due to the highly unstable nature of tris(amine) molybdenum tricarbonyls in solution their reactions with halogen were performed using solid carbonyls. After the dropwise addition of a hexane solution of one equivalent of bromine or iodine the colour of the solid carbonyls turned brown. Evolution of carbon monoxide was not observed during the reaction. The reaction mixture was stirred well and the supernatant liquid was decanted out. After washing with benzene the products were dried *in vacuo*. The IR spectra (Table IV) of the complexes together with conductivity data showed them to be the $[Mo(CO)_3(amine)_3X]X$ derivatives. Since the C–O stretching bands[12] around 1862 and 1709 cm^{-1} were not observed in the spectra of the halogenated products, it was concluded that the halogenated products were free from unreacted $Mo(CO)_3(amine)_3$ derivatives.

TABLE IV. C–O Stretching Frequencies and Molar Conductivity Data of $[Mo(CO)_3(amine)_3X]X$ Derivatives.

Complex	CO Bands (KBr discs) (cm^{-1})		Mol. Cond. (THF) ($ohm^{-1} cm^2$)
$[Mo(CO)_3(C_4H_9NH_2)_3I]I$	2000ms	1922ms	61.6
$[Mo(CO)_3(C_6H_{11}NH_2)_3I]I$	1984s	1898s,br	68.2
$[Mo(CO)_3(C_4H_9NH_2)_3Br]Br$	1990s	1926sh	63.0
$[Mo(CO)_3(C_6H_{11}NH_2)_3Br]Br$	2000ms	1922ms	67.2

Halogenation of (1-Diphenylphosphino-2-diphenylarsinoethane)metal Tetracarbonyls

Bromine or iodine oxidised $M(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ (M = Mo, W) derivatives into the hepta-coordinated $M(CO)_3(Ph_2PCH_2CH_2AsPh_2)X_2$ (X = Br, I). All the complexes were air sensitive and yellow in colour. They were insoluble in aliphatic hydrocarbons and light petroleum (60 °–80 °C) but dissolved in acetone, dichloromethane, benzene. Their infrared spectra exhibited three very strong and one medium to strong bands in the CO region (M = Mo, X = I, ν_{CO}: 2032 vs, 1956 m, 1936 vs, 1862 vs, X = Br, ν_{CO}: 2028 vs, 1938 vs, 1883 vs; M = W, X = I, ν_{CO}: 2032 vs, 1932 vs, 1852 vs, X = Br, ν_{CO}: 2028 vs, 1960 s, 1934 vs, 1852 vs cm^{-1} (KBr discs)). The appearance of an additional medium weak high frequency CO band (2088 cm^{-1}), similar to $[W(CO)_4(Me_2PCH_2CH_2PMe_2)I]I$,[13] in the spectrum of the brominated tungsten carbonyl derivative indicated the possibility of formation of the cationic complex, $[W(CO)_4(Ph_2PCH_2CH_2AsPh_2)Br]Br$ which ultimately changed into the neutral $W(CO)_3(Ph_2PCH_2CH_2AsPh_2)Br_2$ complex. Oxidation of $Cr(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ with iodine yielded the hepta-coordinated ionic complex, $[Cr(CO)_4(Ph_2PCH_2CH_2AsPh_2)I]I$ (ν_{CO}: 2072 s, 1994 s, 1960 m, 1930 m and 1886 cm^{-1}) while the bromination product was of different nature. It was very unstable in the solid state, hence it was extracted in benzene. The IR spectrum of the benzene extract showed two strong bands around 1962 and 1818 cm^{-1}. These frequencies were in close resemblance with the CO frequencies of the known $M(CO)_2(L\text{–}L)X_2$ derivatives. Similarly the oxidation of $M(CO)_4(Ph_2PCH_2CH_2AsPh_2)$ (M = Mo, W) with a hexane solution of chlorine yielded hexacoordinated $M(CO)_2(Ph_2PCH_2CH_2AsPh_2)Cl_2$ derivatives (M = Mo, ν_{CO}: 1960, 1818; M = W, ν_{CO}: 1960, 1818 cm^{-1}).

Experimental

All experiments were performed under dry nitrogen or *in vacuo*. Amine metal pentacarbonyls, bis(amine) molybdenum tetracarbonyls, tris(amine)molybdenum tricarbonyls and (1-diphenylphosphino-2-diphenylarsinoethane)metal tetracarbonyls were prepared by the methods given in literature.[12, 14–17] Infrared spectra were measured on a Perkin–Elmer spectrophotometer Model 221. Conductivity measurements were performed on a Toshniwal conductivity bridge Model 302.

Preparation of Diiodo(butylamine)molybdenum Tetracarbonyl

A hexane solution of iodine (0.17 g in 40 ml) was added dropwise in a solution of (butylamine)molybdenum pentacarbonyl (0.2 g in 30 ml hexane) under nitrogen at room temperature. The reaction mixture was stirred well. The colour of the iodine solution disappeared during addition and a brown precipitate settled down at the bottom of the reaction flask. The supernatant liquid was decanted out under nitrogen and the precipitate was washed well with hexane to remove excess of iodine and any unreacted (butylamine)molybdenum pentacarbonyl. It was identified to be diiodo(butylamine)molybdenum tetracarbonyl (found: C, 16.8; H, 2.3; N, 2.5; I, 49.2. $C_8H_{11}NI_2MoO_4$ calcd: C, 17.9; H, 2.1; N, 2.6; I, 47.4%). Yield 45.8%; 138 °C (dec.). It was insoluble in aliphatic hydrocarbons and light petroleum (60°–80° C) but dissolved in aromatic hydrocarbons, tetrahydrofuran, dichloromethane and acetone.

Preparation of Dibromo(butylamine)molybdenum Tetracarbonyl

Bromine (0.11 g in 20 ml hexane) and (butylamine) molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give brown dibromo(butylamine)molybdenum tetracarbonyl (found: C, 20.8; H, 2.2; N, 3.1; Br, 35.4. $C_8H_{11}NBr_2MoO_4$ calcd: C, 21.7; H, 2.4; N, 3.17; Br, 36.2%). Yield 38.5%.

Preparation of Diiodo(cyclohexylamine)molybdenum Tetracarbonyl

Iodine (0.15 g in 30 ml hexane) and (cyclohexylamine)molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give orange–brown diiodo(cyclohexylamine)molybdenum tetracarbonyl (found: C, 21.2; H, 2.1; N, 2.2; I, 48.5. $C_{10}H_{13}NI_2MoO_4$ calcd: C, 21.3; H, 2.3; N, 2.4; I, 45.2%). Yield 45.4%.

Preparation of Dibromo(cyclohexylamine)molybdenum Tetracarbonyl

Similarly bromine (0.1 g in 20 ml hexane) and (cyclohexylamine)molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give orange–brown dibromo(cyclohexylamine)molybdenum tetracarbonyl (found: C, 24.2; H, 2.5; N, 2.9; Br, 35.8. $C_{10}H_{13}NBr_2MoO_4$ calcd: C, 25.7; H, 2.7; N, 3.0; Br, 34.2%). Yield 40.2%.

Preparation of Diiodo(benzylamine)molybdenum Tetracarbonyl

Iodine (0.15 g in 30 ml hexane) and (benzylamine) molybdenum pentacarbonyl (0.2 g in 30 ml hexane) after reaction at room temperature under nitrogen produced a brown solid, diiodo(benzylamine)molybdenum tetracarbonyl (found: C, 22.3; H, 1.4; N, 2.4; I, 45.7. $C_{11}H_9NI_2MoO_4$ calcd: C, 23.2; H, 1.5; N, 2.4; I, 44.6%) Yield 41.2%.

Preparation of Dibromo(benzylamine)molybdenum Tetracarbonyl

Bromine (0.1 g in 20 ml hexane) and (benzylamine) molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give brown dibromo(benzylamine)molybdenum tetracarbonyl (found: C, 26.5; H, 1.7; N, 2.8; Br, 34.2. $C_{11}H_9NBr_2MoO_4$ calcd.: C, 27.7; H, 1.8; N, 2.9; Br, 33.6%). Yield 38.5%.

Preparation of Diiodo(morpholine)molybdenum Tetracarbonyl

Iodine (0.16 g in 35 ml hexane) and (morpholine) molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give the orange diiodo(morpholine)molybdenum tetracarbonyl (found: C, 16.8; H, 1.5; N, 2.5; I, 47.2. $C_8H_9NI_2MoO_5$ calcd: C, 17.4; H, 1.6; N, 2.5; I, 46.2%). Yield 47.1%.

Preparation of Dibromo(morpholine)molybdenum Tetracarbonyl

Bromine (0.1 g in 20 ml hexane) and (morpholine) molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give the orange dibromo(morpholine)molybdenum tetracarbonyl (found: C, 20.4; H, 1.8; N, 3.0; Br, 36.2. $C_8H_9NBr_2MoO_5$ calcd: C, 21.1; H, 1.9; N, 3.08; Br, 35.1%). Yield 44.3%.

Preparation of Dichloro(morpholine)molybdenum Tetracarbonyl

Chlorine swept benzene was added dropwise into a solution of (morpholine)molybdenum pentacarbonyl (0.2 g in 30 ml hexane) under nitrogen at room temperature. The work up was similar to the isolation of the other products. The isolated product was identified as dichloro(morpholine)molybdenum tetracarbonyl (found: C, 25.2; H, 2.2; N, 3.7; Cl, 20.5. $C_8H_9NCl_2MoO_5$ calcd: C, 26.2; H, 2.4; N, 3.8; Cl, 19.4%). Yield 31.9%.

Preparation of Diiodo(piperidine)molybdenum Tetracarbonyl

Iodine (0.16 g in 35 ml hexane) and (piperidine) molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give the orange diiodo(piperidine)molybdenum tetracarbonyl (found: C, 18.8; H, 2.0; N, 2.4; I, 45.8. $C_9H_{11}NI_2MoO_4$ calcd: C, 19.7; H, 2.0; N, 2.5; I, 46.4%). Yield 52.9%.

Preparation of Dibromo(piperidine)molybdenum Tetracarbonyl

Bromine (0.1 g in 20 ml hexane) and (piperidine) molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give the orange dibromo(piperidine)molybdenum tetracarbonyl (found: C, 22.9; H, 2.3; N, 3.1; Br, 36.5. $C_9H_{11}NBr_2MoO_4$ calcd: C, 23.8; H, 2.4; N, 3.1; Br, 35.3%). Yield 47.1%.

Preparation of Dichloro(piperidine)molybdenum Tetracarbonyl

A benzene solution of chlorine and (piperidine) molybdenum pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give the light orange dichloro(piperidine)molybdenum tetracarbonyl (found: C, 27.8; H, 2.9; N, 3.7; Cl, 20.6. $C_9H_{11}NCl_2MoO_4$ calcd: C, 29.7; H, 3.02; N, 3.8; Cl, 19.4%). Yield 36.3%.

Preparation of Diiodo(cyclohexylamine)chromium Tricarbonyl

A hexane solution of iodine (0.17 g in 40 ml) was added drop by drop in a solution of (cyclohexylamine) chromium pentacarbonyl (0.2 g in 30 ml hexane) under nitrogen at room temperature (~30° C). The reaction mixture was stirred well. No consumption of iodine was observed at this temperature. The reaction mixture was warmed to 40°–50° C for 15 minutes with constant stirring. An yellowish brown turbidity appeared in the reaction mixture. The solvent was removed *in vacuo* and the product washed well with nitrogen saturated hexane to remove excess of the unreacted reactants. The colour of the precipitate began to change gradually into bluish green. At this stage the solid was extracted in benzene which left an insoluble green product. The IR spectrum of the benzene extract was recorded which showed close resemblance with those of the known hexacoordinate $M(CO)_3LX_2$ derivatives.

Similarly prepared were dibromo(cyclohexylamine) chromium tricarbonyl, diiodo(morpholine)chromium tricarbonyl, dibromo(morpholine)chromium tricarbonyl, diiodo(piperidine)chromium tricarbonyl and dibromo (piperidine)chromium tricarbonyl.

Preparation of Diiodobis(cyclohexylamine)molybdenum Tricarbonyl

A hexane solution of iodine (0.14 g in 30 ml) was added dropwise onto solid bis(cyclohexylamine)molybdenum tetracarbonyl (0.2 g) at room temperature under nitrogen with constant stirring. The dissolution of tetracarbonyl took place and a flocculent orange precipitate simultaneously settled down at the bottom of the flask. The solvent was decanted out under nitrogen. The residue was recrystallised from benzene and was identified as diiodobis(cyclohexylamine)molybdenum tricarbonyl (found: C, 27.8; H, 4.2; N, 4.0; I, 41.8. $C_{15}H_{26}N_2I_2MoO_3$ calcd: C, 28.4; H, 4.1; N, 4.4; I, 40.18%). Yield 46.3%.

Preparation of Diiodobis(morpholine)molybdenum Tricarbonyl

Iodine (0.15 g in 30 ml hexane) and solid bis(morpholine)molybdenum tetracarbonyl (0.2 g) reacted at room temperature under nitrogen to give the orange–brown diiodobis(morpholine)molybdenum tricarbonyl (found: C, 20.2; H, 2.8; N, 4.4; I, 42.8. $C_{11}H_{18}N_2I_2MoO_5$ calcd: C, 21.8; H, 2.9; N, 4.6; I, 41.7%). Yield 47.8%.

Preparation of Diiodobis(piperidine)molybdenum Tricarbonyl

Iodine (0.15 g in 30 ml hexane) and solid bis(piperidine)molybdenum tetracarbonyl (0.2 g) reacted at room temperature under nitrogen to give the orange–brown diiodobis(piperidine)molybdenum tricarbonyl (found: C, 24.1; H, 3.5; N, 4.6; I, 43.8. $C_{13}H_{22}N_2I_2MoO_3$ calcd: C, 25.8; H, 3.6; N, 4.6; I, 42.05%). Yield 51.4%.

Preparation of Dibromobis(cyclohexylamine)molybdenum Dicarbonyl

Bromine (.084 g in 20 ml hexane) reacted with solid bis(cyclohexylamine)molybdenum tetracarbonyl (0.2 g) at room temperature under nitrogen. A yellowish orange precipitate which was very unstable settled down at the bottom of the flask. The solvent was decanted out and the product was extracted with benzene. The IR spectrum of this product in benzene resembled the spectra of known $M(CO)_2L_2X_2$ derivatives.

Similarly prepared were dibromobis(morpholine) molybdenum dicarbonyl and dibromobis(piperidine) molybdenum dicarbonyl.

Preparation of Iodotris(butylamine)molybdenum Tricarbonyl Iodide

A hexane solution of iodine (0.127 g in 25 ml) was added dropwise to the solid tris(butylamine)molybdenum tricarbonyl (0.2 g) at room temperature under nitrogen with constant stirring. The colour of solid carbonyl turned brown. The solvent was decanted out under nitrogen and the residue was washed several times with hexane and finally with benzene. It was dried *in vacuo* and identified as iodotris(butylamine) molybdenum tricarbonyl iodide (found: C, 28.1; H, 4.9; N, 6.2; I, 39.4. $C_{15}H_{33}N_3I_2MoO_3$ calcd: C, 27.5; H, 5.05; N, 6.4; I, 38.8%). It was very sparingly soluble in acetone, dichloromethane, tetrahydrofuran and insoluble in aliphatic hydrocarbons, light petroleum (60°–80° C) and benzene.

Preparation of Bromotris(butylamine)molybdenum Tricarbonyl Bromide

Bromine (.08 g in 20 ml hexane) and solid tris(butylamine)molybdenum tricarbonyl (0.2 g) reacted at room temperature under nitrogen to give brown bromotris(butylamine)molybdenum tricarbonyl bromide (found: C, 31.6; H, 5.8; N, 7.2; Br, 29.2. $C_{15}H_{33}N_3Br_2MoO_3$ calcd: C, 32.2; H, 5.9; N, 7.5; Br, 28.6%).

Preparation of Iodotris(cyclohexylamine)molybdenum Tricarbonyl Iodide

Iodine (0.11 g) in 25 ml hexane) and solid tris(cyclohexylamine)molybdenum tricarbonyl (0.2 g) reacted at room temperature under nitrogen to give brown iodotris(cyclohexylamine)molybdenum tricarbonyl iodide (found: C, 33.8; H, 5.2; N, 5.5; I, 35.2. $C_{21}H_{39}N_3I_2MoO_3$ calcd: C, 34.4; H, 5.3; N, 5.7; I, 34.7%).

Preparation of Bromotris(cyclohexylamine)molybdenum Tricarbonyl Bromide

Bromine (.07 g in 20 ml hexane) and solid tris(cyclohexylamine)molybdenum tricarbonyl (0.2 g) reacted at room temperature under nitrogen to give brown bromotris(cyclohexylamine)molybdenum tricarbonyl bromide (found: C, 38.4; H, 5.9; N, 6.4; Br, 26.2. $C_{21}H_{39}N_3Br_2MoO_3$ calcd: C, 39.5; H, 6.1; N, 6.5; Br, 25.1%).

Preparation of Diiodo(1-diphenylphosphino-2-diphenylarsinoethane)molybdenum Tricarbonyl

Iodine (.08 g in 25 ml hexane) and (1-diphenylphosphino-2-diphenylarsinoethane)molybdenum tetracarbonyl (0.2 g in 10 ml benzene) reacted under nitrogen at room temperature to give diiodo(1-diphenylphosphino-2-diphenylarsinoethane)molybdenum tricarbonyl (found: C, 38.8; H, 2.6; I, 30.2. $C_{29}H_{24}I_2O_3MoPAs$ calcd: C, 39.7; H, 2.7; I, 28.9%). It was soluble in acetone, dichloromethane, benzene, carbon tetrachloride but insoluble in aliphatic hydrocarbons and light petroleum (60°–80° C).

Preparation of Diiodo(1-diphenylphosphino-2-diphenylarsinoethane)tungsten Tricarbonyl

Iodine (0.07 g in 25 ml hexane) and (1-diphenylphosphino-2-diphenylarsinoethane)tungsten tetracarbonyl (0.2 g in 10 ml benzene) reacted at room temperature under nitrogen to give the yellowish orange diiodo(1-diphenylphosphino-2-diphenylarsinoethane) tungsten tricarbonyl (found: C, 35.2; H, 2.3; I, 28.1. $C_{29}H_{24}I_2O_3WPAs$ calcd: C, 36.1; H, 2.4; I, 26.3%).

Preparation of Iodo(1-diphenylphosphino-2-diphenylarsinoethane)chromium Tetracarbonyl Iodide

Iodine (0.085 g in 25 ml hexane) and (1-diphenylphosphino-2-diphenylarsinoethane)chromium tetracarbonyl (0.2 g in 10 ml benzene) reacted at room temperature under nitrogen to give the bright yellow iodo(1-diphenylphosphino-2-diphenylarsinoethane) chromium tetracarbonyl iodide (found: C, 40.4; H, 2.6; I, 30.6. $C_{30}H_{24}I_2O_4CrPAs$ calcd: C, 40.8; H, 2.7; I, 29.5%).

Preparation of Dibromo(1-diphenylphosphino-2-diphenylarsinoethane)molybdenum Tricarbonyl

Bromine (.05 g in 25 ml hexane) and (1-diphenylphosphino-2-diphenylarsinoethane)molybdenum tetracarbonyl (0.2 g in 10 ml benzene) reacted at room temperature in nitrogen to yield the yellowish brown dibromo (1-diphenylphosphino - 2 - diphenylarsinoethane)molybdenum tricarbonyl (found: C, 43.2; H, 2.9; Br, 21.8. $C_{29}H_{24}Br_2O_3MoPAs$ calcd: C, 44.5; H, 3.06; Br, 20.4%).

Preparation of Dibromo(1-diphenylphosphino-2-diphenylarsinoethane)tungsten Tricarbonyl

Bromine (0.045 g in 25 ml hexane) and (1-diphenylphosphino-2-diphenylarsinoethane)tungsten tetracarbonyl (0.2 g in 10 ml benzene) reacted at room temperature under nitrogen to give the yellowish orange dibromo(1-diphenylphosphino-2-diphenylarsinoethane)tungsten tricarbonyl (found: C, 39.1; H, 2.6; Br, 19.8. $C_{29}H_{24}Br_2O_3WPAs$ calcd: C, 40.0; H, 2.7; Br, 18.39%).

Preparation of Dibromo(1-diphenylphosphino-2-diphenylarsinoethane)chromium Dicarbonyl

Bromine (0.055 g in 25 ml hexane) and (1-diphenylphosphino-2-diphenylarsinoethane)chromium tetracarbonyl (0.2 g in 10 ml benzene) reacted at room temperature under nitrogen to give a yellow precipitate which was very unstable. The solvent was decanted out and the product was extracted with benzene. The IR spectrum of the benzene extract resembled the spectra of known $M(CO)_2(L–L)X_2$ derivatives.

Similarly prepared were dichloro(1-diphenylphosphino-2-diphenylarsinoethane)molybdenum dicarbonyl and dichloro(1-diphenylphosphino-2-diphenylarsinoethane)tungsten dicarbonyl.

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